

MOLECULAR STRUCTURE AND CHIRALITY DETERMINATION FROM PULSED-JET FOURIER TRANSFORM MICROWAVE SPECTROSCOPY

SIMON LOBSIGER, CRISTOBAL PEREZ, LUCA EVANGELISTI, NATHAN A SEIFERT, BROOKS PATE, KEVIN LEHMANN, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA.*

Fourier transform microwave (FTMW) spectroscopy has been used for many years as one of the most accurate methods to determine gas-phase structures of molecules and small molecular clusters. In the last years two pioneering works ushered in a new era applications. First, by exploiting the reduced measurement time and the high sensitivity, the development of chirped-pulse CP-FTMW spectrometers^a enabled the full structural determination of molecules of increasing size as well as molecular clusters. Second, and more recently, Patterson et al.^b showed that rotational spectroscopy can also be used for enantiomer-specific detection. Here we present an experimental approach that combines both in a single spectrometer. This set-up is capable to rapidly obtain the full heavy-atom substitution structure using the CP-FTMW features. The inclusion of an extra set of broadband horns allows for a chirality-sensitive measurement of the sample.^{c,d} The measurement we implement is a three-wave mixing experiment that uses time-separated pulses to optimally create the chiral coherence – an approach that was proposed recently.^e Using samples of R-, S- and racemic Solketal, the physical properties of the three-wave mixing experiment were studied. This involved the measurement of the corresponding nutation curves (molecular signal intensity vs excitation pulse duration) to demonstrate the optimal pulse sequence. The phase stability of the chiral signal, required to assign the absolute stereochemistry, has been studied as a function of the measurement signal-to-noise ratio using a “phasogram” method.

^aG. G. Brown, B. C. Dian, K. O. Douglass, S. M. Geyer, S. T. Shipman, B. H. Pate, *Rev. Sci. Instrum.* 2008, 79, 053103.

^bD. Patterson, M. Schnell, J. M. Doyle, *Nature* 2013, 497, 475–477.

^cD. Patterson, J. M. Doyle, *Phys. Rev. Lett.* 2013, 111, 023008.

^dV. A. Shubert, D. Schmitz, D. Patterson, J. M. Doyle, M. Schnell, *Angew. Chem. Int. Ed.* 2014, 53, 1152–1155.

^eJ.-U. Grabow, *Angew. Chem.* 2013, 125, 11914 – 11916; *Angew. Chem. Int. Ed.* 2013, 52, 11698 –11700.